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FACULTY OF THE CHEMICAL TECHNOLOGY OF GLASS AND SITALS AT 80 YEARS: YOUTH KNOWS — MATURITY CAN

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The results of research performed in the Faculty of the Chemical Technology of Glass and Sitals at the D. I. Mendeleev Russian Chemical Technology University over the last five years are summarized.

Key words: glass, glass ceramic, structure, properties.

I. I. Kitaigorodskii founded the Faculty of Glass at the D. I. Mendeleev Moscow Chemical Technology University (now D. I. Mendeleev Russian Chemical Technology University) eighty years ago and headed it for more than thirty years. He secured the faculty's critically important role in training scientific cadres and technologists in the field of glass in the USSR, its leading role in the science of glass and glass ceramics and the role of a generator of ideas for the development of new technologies and materials. It is I. I. Kitaigorodskii who happened to lead the work on creating in the USSR a new class of volume crystallized glasses, which he called sital, now a subject of numerous studies.

The Faculty of the Chemical Technology of Glass and Sitals [the Faculty] is still leader in preparing highly trained glassmakers, which is largely due to the work of outstanding successors of I. I. Kitaigorodskii's work — Professor N. M. Pavlushkin and Academician P. D. Sarkisov. The Faculty became the largest scientific center in Russia and is equipped with the newest technological and science-intense equipment, which makes it possible to train cadres with truly the highest qualifications by attracting students to scientific and production work in the teaching-science-production cycle. In the Faculty, efficiently operating scientific laboratories were created together with the All-Russia Scientific-Research Institute of Aviation Materials (VIAM) and N. S. Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences (IONKh), the Center for Optical Glass was founded with the support of Élektrostal', JSC, and the Laboratory for Drawing Glass Fiber and the Laboratory of Laser Technologies were created with the support of the L. Ya. Lavochkin Scientific-Industrial Association. For many years the Faculty has been collaborating closely, including within the framework of special federal programs, with the Obninsk Scientific and Production Association Tekhnologiya (Obninsk) and with the Lytkarino Optical Glass Plant and the Scientific-Research Institute of Technical Glass. The joint efforts of the Faculty and the Bebig, JSC, led to the development of a production line for glass microspheres for nuclear medicine. Students from the entire university and not just from the Faculty have the opportunity to become staff members of these subdivisions on a competitive basis.

During the last two decades the Faculty has repeatedly won competitions set up by Minobrnauki, Minpromtorg, Rosatom, RFFI, INTAS and NATO (Science for Peace Program), MNTTS, Landau-Network-Centro-Volta, Laue-Langevin Institute and other organizations, which made it possible to perform research at the highest international level even during the period of great decline of science in Russia, the so-called hard nineties.

In 2010 the Faculty and Professor Alberto Paleari at Milan University won a competition to obtain a megagrant according to Resolution No. 220 of the Russian Federation on bringing leading scientists to institutions of higher learning in Russia to perform research on "New functional possibilities of glass and glass ceramics." As a result the best equipped laboratory in Russia was created at D. I. Mendeleev Russian Chemical Technology University to perform fundamental research and development work on innovative technologies of glassy and glass ceramic materials with the most diverse applications — in aviation and space engineering, in

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information technologies, laser technology, photonics, instrument building and medicine. In 2012 this laboratory — the Laboratory of Functional Materials [the Laboratory] — was named after the head of the Faculty, Academician of the Russian Academy of Sciences Pavel Dzhibraelovich Sarkisov, who stands at the forefront of its creation. Essentially, today, the Faculty and the Laboratory comprise a unified group in which the process of teaching undergraduate and graduate students under the direction of the most experienced teachers — Professor N. Yu. Mikhailenko and L. A. Orlova and Associate Professor B. I. Beletskii, N. V. Popovich, M. A. Semin, Yu. A. Spiridonova and E. E. Stroganova — is closely intertwined with scientific-research work and innovative developments.

Prominent foreign scientists are participating in the work of the Laboratory: Director of the International Institute New Functionality in Glass Professor H. Jane (USA), Professor T. Komatsu (Technological University of Nagaoka, Japan), Professors E. Fargin and V. Cardinal (University of Bordeaux, France), Professor B. Champagnon (University of Lyon-1, France), Dr. R. Brounch and Professor H. Hessenkemper (Mining Academy, Freiberg, Germany), Doctor of Physical and Mathematical Sciences G. E. Malashkevich (B. I. Stepanov Institute of Physics of the National Academy of Sciences Belarus, Minsk, Belarus), Candidate of Technical Sciences V. I. Savinkov (Ukraine) and others. Professor Alberto Paleari of Milan University is the director of the Laboratory. The Faculty and the Laboratory are integrated into a wide international network of organizations with a corresponding profile, encompassing more than 30 countries.

The technological equipment of the Laboratory makes it possible to synthesize glass on a semi-commercial scale in crucibles up to 15 liters in size, which creates the foundation for successful commercialization of new advances. The following have been created in the laboratory: a batch preparation section, including for making ultrapure glass; a section for making glass and producing optically uniform glass, equipped with high-temperature furnaces, glass mixing machines, bubbling setups, platinum crucible to 5 liters and platinum mixers; a section for making glass at temperatures above 1600°C for nuclear medicine; and, numerous laboratory melting and annealing furnaces. The laboratory possesses new grinding equipment, equipment for precise sieving of micropowder (Retsch Company) as well as precision means for determining the dispersity of powder. The Laboratory possesses a functioning plasmatron, in which glass powder spheroidized, as well as a commercial setup for drawing glass ribbon. Modern equipment is available for mechanical working of samples and evaluating the state of a surface using a profilograph-profilometer and for thermal poling, ion-exchange hardening, hot pressing, crystallization in a temperature gradient field, and so forth.

The science-intensive equipment in the Faculty and the Laboratory includes the following: LEA-S500 laser elemental composition analyzer and iCAP-Q mass-spectrometer with inductively coupled plasma, STA 409 F3 synchronous thermal analyzer (Netzshch Company), D2 Bruker AXS x-ray powder diffractometer, JEOL-651-LV scanning electron microscope, DIL402PC dilatometer (Netzshch Company), facility for measuring the mechanical properties of materials (Shimadzu Company), MS3504i spectral-analytical complex based on a monochromator/spectrograph, Shimadzu UV-3600 spectrophotometer, INTEGRA SPECTRA Raman light scattering spectrometer with a high-resolution confocal microscope coupled with an atomic force microscope; complex for studying the optical and nonlinear optical properties of materials at temperatures to 1500°C (using a LinKam high-temperature table), and a TETA-X femtosecond laser complex with a radiation diagnostics and positioning system.

The Faculty and Laboratory staff uses extensively the method of low-angle thermal neutron scattering to test the nonuniform structure of glass on the scale 1 – 100 nm (high-flux reactor at the Laue-Langevin Institute, France). A recently acquired information-search system SciGlass Software Suite produced by LHASA, LLC (USA) includes the most complete information on the properties of glasses and methods for obtaining them. The SciGlass system makes it possible to shorten considerably the initial stages of synthesis. At the same time it is becoming a unique teaching tool for training specialists in the field of glass. This information-search system was not available in Russia in the past.

The scientific subject matter studied in the Faculty cover a wide range of fundamental problems of the glassy state and nano- and microscale modifications of the structure of glass and provides for the creation of materials for different purposes ranging from optical to bioactive. The Laboratory plans include development of the scientific principles of a new technology — the technology of nanostructured glasses of optical quality, i.e., uniform on a scale of the order of 0.5 – 1 μm or more but containing phase nonuniformities about 30 nm in size, distributed in the volume or on the surface of glass according to a law prescribed by the developer.

The articles published in this issue of the journal provide information on developments and research by staff, graduate students and students in the Faculty and the Laboratory in the field of optical materials science and photonics, glasses, sitals and composites for the aviation and space industry, medicine, the construction materials industry, and so on. The present article briefly describes the advances made in the last several years.

NEW FUNCTIONAL MATERIALS BASED ON OPTICAL AND NANOSTRUCTURED GLASSES

The possibility of obtaining uniform glasses with special functional properties in small volumes opens the way to innovative developments where, considering the miniaturization of optical devices, there is an acute need for modern instrument building. It requires the use of an increasingly lon-

ger list of glasses with different spectral and functions characteristics.

We have developed a series of optically uniform glasses — glasses with miniaturized nonuniformity on the nano- and microscales (laser phosphate glass, magneto-optical glass, boron-germanate glasses co-activated by Er^{3+} and Yb^{3+}, aluminum borate glasses containing rare-earth elements (REE) and others) and glasses in which amorphous or crystalline nano-nonuniformities were formed in a controllable manner.

It has been shown for the example of neodymium-activated laser phosphate glass that the technological resources of the Laboratory permit synthesizing optically uniform glasses in platinum vessels from 300 ml to 5 liters in size with 400×200×50 mm uniform castings (see photo on the cover). The laser glass obtained [1] is distinguished by low concentration quenching of the luminescence with decay time $\tau = 295$ μsec at Nd^{3+} concentration 3.5×10^{20} ions/cm^3, improved thermo-optical characteristics ($dn/dt = 6 \times 10^{-6}\ K^{-1}$), high radiant strength and ultralow coefficient of inactive absorption ($a_{1053} = 0.0009\ cm^{-1}$), i.e., in terms of its properties it is on par with or even surpasses the best commercial laser systems.

Colorless optical quality glasses with very high molar content of REE oxide (Tb_2O_3 to 31%), which are efficient magneto-optical shutters and Faraday phase shifters, have been obtained in small volume crucibles (to 500 ml). The Verdet constant of this glasses [2, 3] at wavelength 633 nm approaches $0.4\ '/(cm \cdot Oe)$, while the absorption coefficient was lowered to $0.001\ cm^{-1}$, which made it possible to obtain record high magneto-optical Q-factor $Q_{1064} = 108\ '/Oe$, almost twice that of commercial magneto-optical glasses.

Intense luminescence of Er^{3+} ions in the spectral region 1.54 μm was found in glasses of the boron-germanate systems with high erbium and yttrium oxide content. In addition a characteristic of the glasses obtained is relatively weak clusterization of erbium: no appreciable quenching of luminescence in the transition $^4I_{13/2} \rightarrow {}^4I_{15/2}$ at Er_2O_3 molar content to 3% was observed [4, 5]. These glasses are promising for use as active elements of miniature solid-state and fiber lasers and laser microswitches.

A high-efficiency light filter, suppressing parasitic modes of a neodymium laser based on borate glass with Sm_2O_3 molar content to 25% and characterized by high transmission in the absorption range of Nd^{3+} ions and linear absorption coefficient for light about $30\ cm^{-1}$ at $\lambda \approx 1.06$ and 1.34 μm, was developed and patented.

Together with optically uniform glasses, we are devoting a great deal of attention to the nano- and microstructuring of glass — controllable formation of amorphous and crystal-like nanostructures in glass, which radically affect the concentration quenching of luminescence in glasses, the appearance and development of quadratic optical nonlinearity and the possibility of developing hybrid glass/crystal structures with unusual combinations of properties.

We use two main approaches to increase the luminescence efficiency of glasses activated separately by transition and rare-earth ions: 1) formation of phase nonuniformities of a crystal nature in oxide glasses, combining in a single material the optical properties of the crystalline phase and the advantages of a glass matrix [7 – 9]; 2) formation in the glass of hantite- like nanostructures of lanthanide aluminum borates with increased Ln–Ln separation [10 – 12]. Both directions are described in greater detail in articles published in the present issue. Here we wish to underscore that we have obtained the first in the world optically uniform glasses in which subsequent heat-treatment can be used to induce a nano-nonuniform structure while retaining uniformity on macro- and microscales. Recently, a nanostructure fiber luminescing in the near-IR region was obtained from Ga_2O_3 blanks containing silicate-germanate glass, co-activated by nickel, at the Scientific Center for Fiber Optics of the Russian Academy of Sciences [13]. In the same glasses but with no activator, luminescence was observed in the blue region of the spectrum and conversion of UV radiation in the visible range was demonstrated. These glasses will serve as a basis for UV radiation sensors in commercial setups, medical instruments and open flames. Patent applications for glass with this composition have been filed in Russia, Italy and the European Union.

It appears that the most promising strategy to obtain high quadratic optical nonlinearity in glasses is to form in their interior ferroelectric nano- and microcrystals, which as a rule possess high optical nonlinearity. In such systems it is promising to use thermal poling, whose possibilities in forming quadratic optical nonlinearity in uniform glass are limited.

The micro- and nanostructured materials obtained [14 – 16], first and foremost, on the basis of the systems $Me_2O–Nb_2O_5–SiO_2$ (Me = Li, Na, K) and $La_2O_3–B_2O_3–GeO_2$ with precipitation, correspondingly, of the ferroelectrics $LiNbO_3$ and $LaBGeO_5$, are promising objects for use in thermal poling, which is expected to permit obtaining fundamentally larger and thermally stable quadratic nonlinearity in glasses [17 – 18], opening up the prospects for effective application of polarized nano-nonuniform glasses in planar and fiber electro-optical transducers operating on the Pockels effect.

To achieve high cubic optical nonlinearity in oxide glasses we have proposed a method that makes it possible to obtain optical quality colorless glass with elevated content of 2 – 3 nm gold nanoparticles [19].

LOCAL CRYSTALLIZATION OF GLASSES BY LASER RADIATION

Local crystallization of glass by laser radiation with the precipitation of functional crystals with non-linear optical or luminescence properties in the form of structures with complex architecture on micro- and nanoscales is a new and very topical problem of optical materials science.

A unique laboratory, the only one of its kind, has been created at the D. I. Mendeleev Russian Chemical Technology University. Here an entire complex of lasers with strongly differing radiation characteristics, ranging from continuous wave to femtosecond with wavelengths from UV to far-IR range, is used to solve problems of local crystallization of glass. The complex includes conventional, for studies of this kind, sources of continuous wave radiation — high-power Nd^{3+}:YAG laser, CO_2 lasers, argon laser — as well as a pulsed copper-vapor laser (in collaboration with the company that manufactures these lasers the Scientific-Industrial Enterprise VELIT) and an ytterbium femtosecond regenerative amplifier with wavelength 1029 nm, the first such lasers used by us for problems of this kind, combining high pulse energy (to 120 kJ) with high pulse repetition frequency (to 25 kHz).

We have obtained different kinds of structures in a glass matrix — from quasicrystalline waveguides to surface microcrystals and volume nanocrystalline structures.

A method of nanocrystallization of gallium-germanium-silicate glasses with formation of luminescing waveguides has been developed [20]. This method is fundamentally new from the standpoint of methodology (formation of functional properties by local laser nanocrystallization of glass) and the result (obtaining transparent luminescing waveguides in glass that does not luminesce). For the first time copper vapor lasers have been used to obtain bulk nanocrystalline structures in glass (mol.%): 7.5 Li_2O, 2.5 Na_2O, 20 Ga_2O_3, 35 GeO_2, 35 SiO_2 with 0.1 – 0.5% NiO added, which possess wide-band luminescence in the near-IR region (the maximum effect is reached at about 1300 – 1350 nm), while preserving the transparency of the glass. Photoluminescence, which is absent in uniform glass, arises because most of the Ni^{2+} ions migrate into nanocrystals. It has been shown that nanocrystallization is accompanied by an increase of the refractive index, which makes it possible to use laser-formed nanostructured channels as active waveguides — the foundations for integrated laser amplifiers or generators, which we plan to develop in the future.

It proved possible to obtain large masses of nonlinear optical microcrystals and quasi-single-crystalline waveguides (Nd, La)$BGeO_5$ and (Sm, La)$BGeO_5$ in glasses with the same composition, lowering in the process the concentration of Nd^{3+} and Sm^{3+} ions [21] (previously introduced by researchers only as absorbing additions for laser heating) by a factor of 5 – 10 and driving it to a level where concentration quenching is low and the medium combines nonlinear optical and luminescent properties, which can be used for the development of integrated waveguide amplifiers and lasers with second-harmonic generation.

Professor T. Komatsu (Technological University of Nagaoka, Japan) working in collaboration with the Laboratory was able to develop a method of forming surface quasi-single-crystalline Eu^{3+}-doped $LiNbO_3$ waveguides in which nonlinear optical and luminescence properties are combined.

Studies of controlled local growth of gold nanoparticles in a multicomponent optically uniform phosphate glass with a high concentration of gold nanoparticles, which makes it possible to increase the cubic optical nonlinearity of transparent glass, have been done [19]. At present the effect on gold-doped glass of femtosecond laser radiation for local growth of nanoparticles in the interior of the glass is being studied.

NEW FUNCTIONAL GLASS CERAMIC AND COMPOSITE MATERIALS WITH HIGH OPERATING TEMPERATURES

The work in this direction, headed by Professor L. A. Orlova, is related first and foremost with real problems of the domestic aviation and space industries and the need to develop functional materials — glass ceramics, protection coatings, composites — with much higher operating temperatures and special dielectric properties.

High-Temperature Glass Ceramic

Specialists in the Faculty have proved experimentally that the most promising direction that combines high operating temperatures and radio transparency is to develop materials based on high-temperature glass ceramic with strontium-anortite composition and very low dielectric permittivity, which combine high values of the deformation temperature ($\geq$ 1300°C) with high stability of thermal, mechanical and dielectric properties in the temperature interval 20 – 1200°C [22 – 25]. A complex study of the thermophysical, mechanical and dielectric properties in a wide temperature interval has been performed at the Federal State Unitary Enterprise ONPP Tekhnologiya for the optimal composition of strontium-anortite glass ceramic. This study showed that with respect to thermal stability, deformation temperature, temperature stability of the thermal and dielectric characteristics this ceramic significantly surpasses the radio transparent glass ceramic currently used in Russia. A prototype production line is to be developed at ONPP Tekhnologiya. Its adoption is a necessary condition for the development of aircraft construction and the space industry in Russia.

High-Temperature Protective Coatings

A sol-gel technology has been developed for high-temperature (above 1400°C) glassy and glass ceramic protective coatings, resistant to attack by different media (oxidative, moist, alkali-metal salts) for SiC-containing materials. Protective high-temperature yttrium-aluminum-silicate (YAS) coatings have been synthesized for ceramo-matrix composites of the type SiC/SiC, whose mechanical properties make them most promising for fabricating assemblies and parts for aviation and space engineering and heat-loaded systems operating under extreme conditions. The tests showed that

YAS coatings deposited on carbide-ceramic substrates have good oxidative resistance at temperatures 1600 – 1650°C and chemical resistance to water vapor and salt Na_2SO_4 in the temperature interval 1300 – 1450°C. These coatings open the possibility of using SiC containing materials at higher temperatures with exposure to oxidative and other aggressive media, which requires aviation-space technology and thermal and nuclear power [26 – 27]. At VIAM there are plans to organize a section for deposition of yttrium-aluminum-silicate coatings on articles fabricated on the basis of silicon carbide.

Composites Based on High-Temperature Glass Ceramic

High-temperature composites with enhanced strength and dielectric characteristics based on a glass ceramic aluminum-silicate matrix with different discrete carbide and nitride fillers (BN, Si_3N_4, SiC and TiC) have been synthesized by hot pressing and their functional properties, reported in greater detail in this issue of the journal, have been investigated [28].

Potassium Niobate Based Ferroelectric Ceramic Obtained from Amorphous Precursor

The original method of obtaining a ferroelectric ceramic from amorphized potassium niobate is described in detail in [29 – 30] and in the corresponding article in the present issue. The glass ceramic approach will be extended to an extensive set of systems with polar phases, in which the production of a densely sintered ceramic is problematic.

Bioactive Materials for Bone Endoprostheses Based on Calcium-Phosphate Systems

Work in this direction, headed by Professor N. Yu. Mikhailenko, is dedicated to the development and investigation of glass ceramic biocompatible resorbable calcium-phosphate materials (simple, in the form of coatings or biopolymer composites), specifically, structuring of the pore space at the macro level and development of highly porous, glass ceramic, biocompatible materials for bone implantology (see [31 – 34] and the article in the present issue of this journal). Previously, Assistant Professor B. I. Beletskii developed the biocomposite material BAK-1000, which has successfully passed all manner of tests and is registered in the Register of State Standards of the Russian Federation and recommended by the Health Ministry of the Russian Federation for serial production and clinical application in Russia. The composite BAK-1000 comprises a microporous framework built from a hydrophilic silicate matrix, in which a resorbable phosphate phase — hydroxyl apatite or hydroxyl apatite combined with tricalcium phosphate — is dispersed. In terms of the composition, pore structure and properties this material is close to the mineral matrix of spongy bone tissue, which secures completely infiltration of it by the tissue liquid of the organism followed by colonization of the open cells by bone cells.

Heat-Protective Coatings for Solar Batteries and Radiators in Spacecraft

A technology for drawing enhanced strength ribbon from radiation-resistant glass for heat-regulating coatings of solar batteries and spacecraft control systems has been developed. Ground-based and flight tests have been successfully passed. In 2013 serial production of ribbon for Roskosmos was organized within the framework of the small investment enterprise TSOS, JSC, created at the Laboratory.

Spheroidized Glassy Materials for Nuclear Medicine

A prototype line for melting, producing, comminuting, size grading and spheroidization of glasses for nuclear medicine has been developed. A technology has been developed for glassy microspheres based on the system Y_2O_3–Al_2O_3–SiO_2 with different compositions and sizes, including monodisperse distribution with a nano or micro surface layer containing no radioactive isotopes. Microspheres made from yttrium-aluminum-silicate glass with elevated molar content of Y_2O_3 (to 23%) have been developed and patented [35 – 37]. A registration certificate has been obtained from Roszdravnadzor; this permits production, sale and medical application on the territory of Russia; and, the first operations have been completed. Borosilicate microspheres with regulated porosity have been developed.

The Laboratory, which is the first and in Russia the only developer and manufacturer of glassy microspheres for treating cancer, capable of fully meeting Russia's needs for radioactive preparations widely used in the West. The work "Glassy microspheres for nuclear medicine" has been recognized as the best innovation exhibit at the 3rd International Forum on Intellectual Property EXPOPRIORITY 2011 (Moscow, Expocenter, 7 December 2011) and was awarded the forum's Grand Prize. Subsequent development of local cancer therapy and methods of diagnostics is tied to the development of porous microspheres with high specific radioactivity and low porosity and combining β- and γ-emitting radioisotopes. The production organization for glass microspheres for nuclear medicine makes it possible to develop in our country a new medical subfield for out-patient cancer treatment, accessible to the public in Russia, by methods of local radiation therapy.

Undergraduate and graduate students at the university, who comprise an absolute group majority, participate in all the studies listed above and many others as well as in the development work. About 70% of the cadres at the Laboratory are young specialists, undergraduate and graduate students at D. I. Mendeleev Russian Chemical Technology University, mainly in the Faculty. The Laboratory's thematic polyphony,

which comes from the diversity of needs for glassy materials, provides adequate financing and security for the best young specialists at D. I. Mendeleev Russian Chemical Technology University. The technological equipment is an excellent trampoline for commercializing the Laboratory's developments, fulfilling at the same time the role of teaching stands on which students at the university obtain a unique possibility of participating in developments at a world level. Working in direct contact with prominent Russian and foreign scientists, having available the most up to date equipment, participating in the solution of fundamental problems of the glassy state, developing truly 21st century materials, publishing in prestigious domestic and foreign journals, our undergraduate and graduate students grow into extra-class specialists. Among them are recipients of President of the Russian Federation grants, RFFI grants ("My first grant" program), Grand Prize at the 3rd International Forum on Intellectual Property, Gold Medal at the International Forum "High technologies of the 21st century", and laureates of many youth competitions. There is every reason to believe that young candidates of science — N. V. Golubev, E. V. Lopatina, S. V. Lotarev, E. Kh. Mamadzhanova, V. S. Ryzhenkov, V. I. Savinkov — and talented graduate students and undergraduate students in the Faculty (G. Atroshchenko, E. Ignat'eva, N. Klimenko, I. Kolokol'chikov, A. Lipat'ev, A. Chainikova, G. Shakhgil'dyan, T. Gel'manova, M. Zeyatdinova, A. Plotnikova, A. Stepko, S. Fedotov, D. Chertin, D. Shevyakina and many others) will determine the course of glass science in Russia in the 21st century and glorify the scientific school of Kitaigorodskii – Pavlushkin – Sarkisov, which traditionally was always sincerely interested in science, the intellect and industriousness, honest, open and happy friendship.

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